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Mathematical Modelling for Copper and Lead Adsorption on Coffee Grounds

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Abstract. Research studies on the adsorption kinetics are conducted in order to determine the absorption time of heavy metals on coffee grounds from liquid. The models of adsorption kinetics and adsorption diffusion are based on mathematical models (Cho *et al.* 2005). The adsorption kinetics can provide information on the mechanisms occurring between adsorbates and adsorbents and give an understanding of the adsorption process. In the mathematical modelling of processes, Lagergren's pseudo-first- and pseudo-second-order kinetics and the intra-particle diffusion models are usually applied. The mathematical modelling has shown that the kinetics of the adsorption process of heavy metals (copper (Cu) and lead (Pb)) is more appropriately described by the Lagergren's pseudo-second-order kinetic model. The kinetic constants ($k_{2Cu} = 0.117$; k_{2Pb} = 0,037 min^{-1}) and the sorption process speed (k_2q_{eCu} = 0.0058–0.4975; k_2q_{ePb} = 0.021–0.1661 mg/g per min) were calculated. After completing the mathematical modelling it was calculated that the Langmuir isotherm better reflects the sorption processes of copper (Cu) ($R^2 = 0.950$), whilst the Freundlich isotherm – the sorption processes of lead (Pb) ($R^2 = 0.925$). The difference between the mathematically modelled and experimentally obtained sorption capacities for removal of heavy metals on coffee grounds from aqueous solutions is 0.059–0.164 mg/l for copper and 0.004–0.285 mg/l for lead. Residual concentrations of metals in a solution showed difference of 1.01 and 0.96 mg/l, respectively.

Keywords: mathematical modelling, coffee grounds, adsorption, copper, lead, heavy metals.

Conference topic: Environmental protection.

Introduction

During the adsorption process, the concentration of metals on a sorbent surface constantly increases until a dynamic equilibrium is reached. It is highly likely that the sorption material has a finite number of sorption sites, thus after sorption capacity reaches its maximum threshold the concentration in the solution ceases to decrease. This dependency is perfectly represented by a function of metal concentration and sorption capacity which shows how metal ions are distributed between adsorbent surface and liquid phase, when there is a constant temperature and pH. The function graph is known as adsorption isotherm (Cho *et al.* 2005; Argun *et al.* 2007; Foo, Mameed 2010).

Throughout the long years of research many different isotherm equations have been developed (Langmuir, Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, etc.), all of which were formulated on the basis of three main methods. In the first case (which takes into account the adsorption kinetics), the adsorption equilibrium is defined as a dynamic system with both the adsorption and desorption rates being equal. The second case involves the adsorption thermodynamics. The third method is based on the analogy of parameters of typical curve plotted during the course of the research study when creating a model (Malek, Farooq 1996). In the practice of modelling of the adsorption processes, the Langmuir and Freundlich isotherms are most commonly used.

Methodology

The modelling of the kinetic parameters of sorption is conducted with the use of mathematical models in order to determine the absorption time of metals from liquid. In practice, the interpretation of adsorption kinetics involves using the described models. For the purposes of mathematical modelling of the adsorption process kinetics, the Lagergren's pseudo-first- and pseudo-second-order kinetic (linear) equations shall be applied.

The main objective in determining the adsorption process kinetics is to determine the values of adsorption rate constants (k_1, k_2) in the Lagergren's pseudo-first- and pseudo-second-order kinetic equations:

$$k_1 = \frac{-2.303\left(\log\left(q_e - q\right) - \log\left(q_e\right)\right)}{t}; \tag{1}$$

$$k_2 = \frac{1}{q_e^2\left(\frac{t}{q} - \frac{t}{q_e}\right)}, \tag{2}$$

where: q_e is the amount of metal adsorbed per unit mass at sorption equilibrium, mg/g; q is the amount of metal adsorbed per unit mass after a certain period of time, mg/g; t is time, min; k_1 and k_2 are adsorption rate constants.

The kinetic parameters are calculated on the basis of the experimental results obtained by applying different concentrations of metals and adsorbent dosage. The sorption capacities yielded during the modelling were later compared with the experimental results, simultaneously studying the influence of time on the sorption process.

Mathematical modelling of the process is carried out using the Langmuir and Freundlich models. The Langmuir sorption isotherm is drawn using the Alfisol LMMpro (Version 1.06) software package.

During the modelling of the sorption process parameters, data input prompt is filled in with the results for sorption capacity determination that were obtained from the experimental studies (when the adsorbent mass is 1.0 g). The Freundlich model parameters are obtained by solving a linear sorption process equation. After establishing that the sorption process takes place in accordance with the Langmuir model and its parameters, the sorbent thrust efficiency was evaluated (Mocevičiūtė 2014):

$$K_R = \frac{1}{1 + k_L C_{init.}} 100\%, \tag{3}$$

where: K_R is the irreversibility co-efficient of the Langmuir isotherm, %; k_L is the Langmuir constant; $C_{init.}$ is the initial concentration of metal in a solution, mg/l.

Results and discussion

The calculations of Lagergren's pseudo-first-order equation parameters made during the modelling of sorption kinetic parameters are shown in Table 1. The calculations are based on dependencies between 3 different concentrations (10; 50; 100 mg/l) and adsorbent amounts (0.5; 1.0; 1.5 g) obtained from the experimental studies.

Table 1. Lagergren's pseudo-first-order kinetic equation parameters for adsorption process (T = 20 °C, t = 60 min)

Heavy metals	$m_{ads.}$	$C_{init.}$, mgl	$qe_{exp,}$, mg/g	$qe_{calc.}$, mg/g	k_1, min^{-1}	k_1q_e, mg/g·min	R^2
Copper (Cu)	0.5	10	0.616	0.256	0.010	0.0060	0.8576
		50	0.980	0.893	0.020	0.0197	0.6094
		100	1.356	1.360	0.059	0.0806	0.4574
	1.0	10	0.473	0.293	0.012	0.0056	0.7498
		50	0.525	0.403	0.014	0.0076	0.6984
		100	0.888	0.890	0.057	0.0508	0.4591
	1.5	10	0.524	0.254	0.010	0.0031	0.7883
		50	0.505	0.234	0.010	0.0100	0.7958
		100	0.750	0.663	0.018	0.0605	0.6301
Lead (Pb)	0.5	10	0.628	0.338	0.004	0.0022	0.9390
		50	1.150	1.126	0.007	0.0082	0.8875
		100	1.700	1.582	0.012	0.0205	0.3665
	1.0	10	0.543	0.508	0.006	0.0031	0.9327
		50	0.773	0.770	0.009	0.0070	0.8283
		100	1.253	1.243	0.019	0.0236	0.6254
	1.5	10	0.539	0.509	0.006	0.0032	0.9282
		50	0.584	0.565	0.007	0.0038	0.9080
		100	1.086	1.060	0.015	0.0167	0.6788

The calculation results shown in Table 1 indicate that at low (10 mg/l) initial concentration of metals in a solution the calculated sorption capacities $qe_{calc.}$ for removal of copper and lead are, respectively, 2.41–1.61 and 1.86–1.06 times lower than those determined experimentally. At higher (50; 100 mg/l) concentrations of metals the calculated sorption capacities for Cu and Pb are almost equal to those obtained from the experimental studies. The determination coefficient R^2 is equal to 0.3665–0.9390. It was found that the initial adsorption speed k_1q_e is 0.0031–0.0806 mg/g per min for removal of copper and 0.022–0.0236 mg/g per min for lead. Accordingly, the average values of the adsorption rate constants k_1 are 0.023 and 0.009 min^{-1}. Table 2 shows calculations for the Lagergren's pseudo-second-order adsorption kinetic equation parameters.

Table 2. Lagergren's pseudo-second-order kinetic equation parameters for adsorption process (T = 20 °C, t = 60 min)

Heavy metals	$m_{ads.}$	$C_{init.}$, mg/l	$qe_{exp.}$, mg/g	$qe_{calc.}$, mg/g	k_2, min^{-1}	k_2qe, mg/g·min	R^2
Copper (Cu)	0.5	10	0.616	0.606	0.009	0.0058	0.9933
		50	0.980	0.962	0.028	0.0272	0.9574
		100	1.356	1.335	0.367	0.4975	0.8509
	1.0	10	0.473	0.463	0.019	0.0092	0.9975
		50	0.525	0.514	0.024	0.0128	0.9916
		100	0.888	0.871	0.553	0.4910	0.8510
	1.5	10	0.524	0.515	0.013	0.0068	0.9965
		50	0.505	0.493	0.012	0.0061	0.9947
		100	0.750	0.731	0.030	0.0224	0.9680
Lead (Pb)	0.5	10	0.628	0.616	0.086	0.0539	0.9183
		50	1.150	1.133	0.097	0.1118	0.8844
		100	1.700	1.674	0.098	0.1661	0.8417
	1.0	10	0.543	0.531	0.004	0.0022	0.9451
		50	0.773	0.760	0.006	0.0050	0.9891
		100	1.253	1.232	0.019	0.0236	0.9654
	1.5	10	0.539	0.528	0.004	0.0022	0.9478
		50	0.584	0.571	0.004	0.0026	0.9590
		100	1.086	1.062	0.014	0.0152	0.9860

The calculation results shown in Table 2 indicate that the calculated sorption capacities $qe_{calc.}$ for removal of both copper and lead are very close (having difference of 0.009–0.026 mg/l) to the sorption capacities $qe_{exp.}$ determined experimentally. The determined initial adsorption speed k_2q_e is 1.87–6.17 and 1.01–4.91 times higher for removal Cu and Pb respectively than when using Lagergren's pseudo-first-order model. Accordingly, the adsorption speed is 0.0058–0.4975, and 0.021–0.1661 mg/g per minute and the average values of the adsorption rate constants k_2 are 0.117 and 0.037 min^{-1}. The accordance of the kinetics of sorption process on coffee grounds with the mathematical model can be represented by dependencies between sorption capacity (experimental and modelled) and time using the experimental results for influence of time on the sorption processes (Figs 1 and 2).

Figure 2 demonstrates that under the Lagergren's pseudo-first-order kinetic model the sorption capacity for removal of copper is higher by 0.83–0.912 mg/g than the experimentally determined sorption capacity (when the initial solution conc. is 10 mg/l and the adsorbent mass is 1 g). The calculations in accordance with the Lagergren's pseudo-second-order kinetic equation show that the experimental sorption capacity is higher by 0.102–0.260 mg/g than the modelled capacity. However, these calculated values are much closer to the experimentally obtained values than the calculated sorption capacities in the first case (under the Lagergren's pseudo-first-order).

The dependencies of sorption capacities for removal of lead from solutions (Fig. 2) are distributed in accordance with the same principle: the modelled sorption capacity is higher by 2.482–2.708 mg/g as per Lagergren's pseudo-first-order equation and lower by 0.324–0.423 mg/g as per Lagergren's pseudo-second-order equation than the sorption capacity determined experimentally. The results of the mathematical modelling of sorption kinetics lead to the conclusion that Lagergren's pseudo-second-order adsorption kinetics model better describes the adsorption kinetics of copper and lead when using coffee grounds as a sorbent.

The modelling of adsorption process yielded the Freundlich and Langmuir isotherm data for copper (Cu) and lead (Pb) which are presented in Table 3. Figure 3 shows the comparison between Freundlich and Langmuir isotherms and experimentally obtained results for copper (Cu).

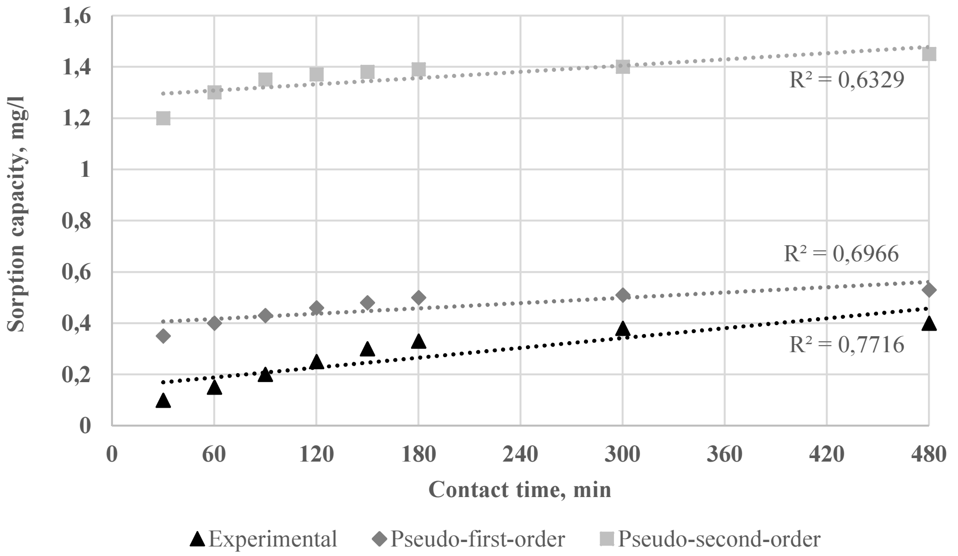

Fig. 1. The dependency of modelled and experimental sorption capacities for removal of copper (Cu) on contact time (T = 20 °C; $C_{init.}$ – 10 mg/l; $m_{ads.}$ – 1 g)

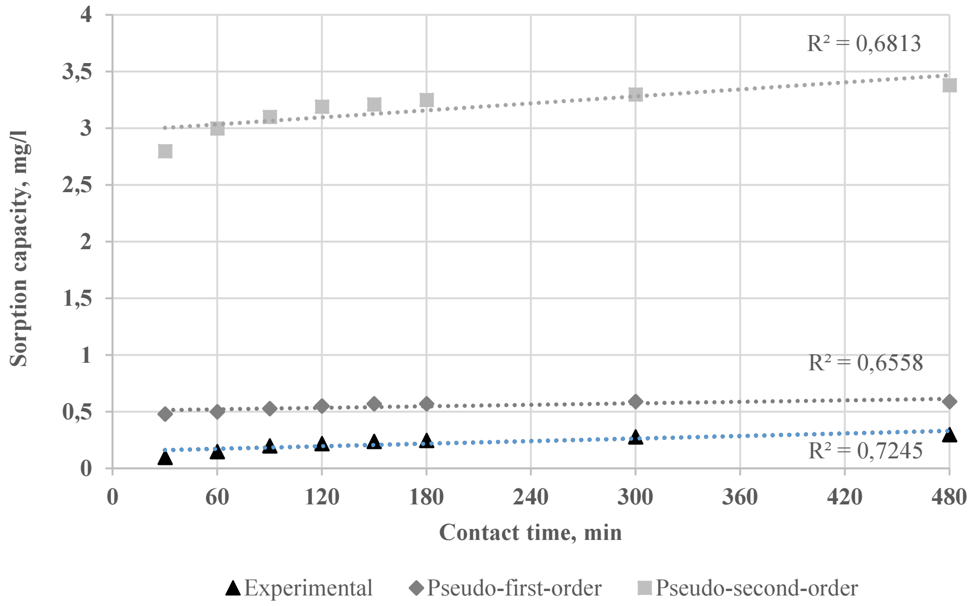

Fig. 2. The dependency of modelled and experimental sorption capacities for removal of lead (Pb) on contact time (T = 20 °C; Cinit. – 10 mg/l; mads. – 1 g)

Table 3. The modelled Freundlich and Langmuir isotherm data

Heavy metals	Langmuir model			Freundlich model		
	k_L	Q_m	R^2	k_F	n	R^2
Copper (Cu)	0.0595	0.9083	0.950	0.0946	−1.738	0.842
Lead (Pb)	0.0198	2.041	0.884	0.1737	−1.380	0.925

Figure 3 indicates that experimental result estimates for copper do not ideally match either of isotherms. The calculated values of the determination co-efficient indicate that the Langmuir isotherm ($R^2 = 0.950$) better reflects the occurred sorption process than the Freundlich isotherm ($R^2 = 0.842$).

The graph comparing the experimental results and the modelled Freundlich and Langmuir isotherms for lead (Pb) is depicted in Figure 4.

The analysis of the experimental values for lead biosorption as illustrated in Figure 4. shows that they are very close to the Freundlich isotherm values. The values of the determination co-efficient also indicate that the Freundlich isotherm ($R^2 = 0.925$) better reflects the sorption process of Pb than the Langmuir model ($R^2 = 0.884$). It can be concluded that the Langmuir isotherm more accurately reflects the sorption processes of copper (Cu) and the Freundlich isotherm – that of lead (Pb). During the sorption of both Pb and Cu ions, it was calculated that the average sorbent thrust efficiency is 35.74%. In the analysis of the mathematical modelling data it is important to compare the experimental and modelled values. Table 4 shows mathematically modelled and experimentally obtained values for sorption capacity and residual concentration. The data in Table 4 indicate that the mathematically modelled values are close to the experimentally obtained values. The modelled sorption capacity values differ from the experimentally determined sorption capacity by 0.059–0.164 mg/l in case of removal of copper and by 0.004–0.285 mg/l in case of lead. Figures 6 and 7 show graphs comparing experimental and mathematically modelled data for the residual concentration of metals.

Figures 5 and 6 reflect the fact that the average difference between the experimental residual concentration $C_{Lexp.}$ and the modelled $C_{Lmod.}$ is 1.01 mg/l in the first case and is 0.96 mg/l in the second case. It can be concluded that the applied mathematical modelling sufficiently reflected the experimental data.

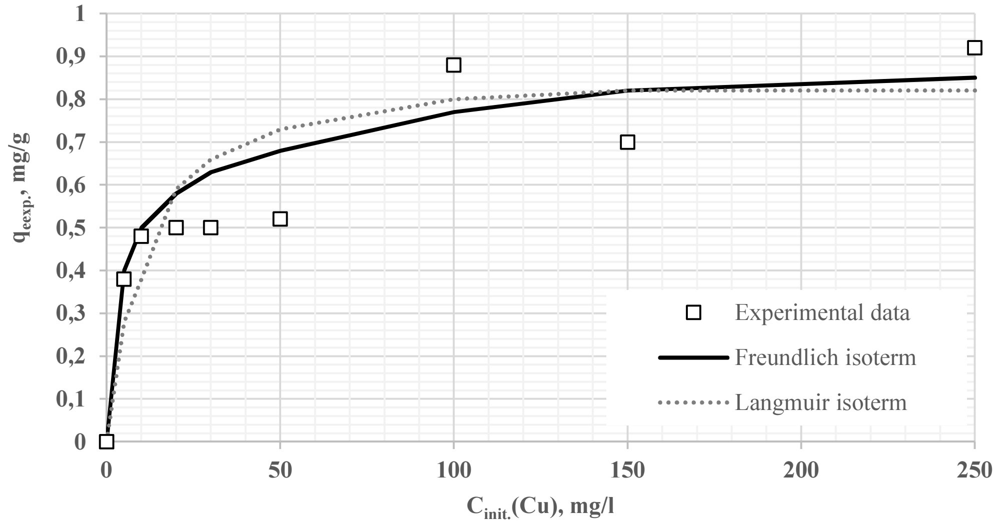

Fig. 3. The comparison between the Langmuir and Freundlich isotherms and the experimental results for copper (Cu)

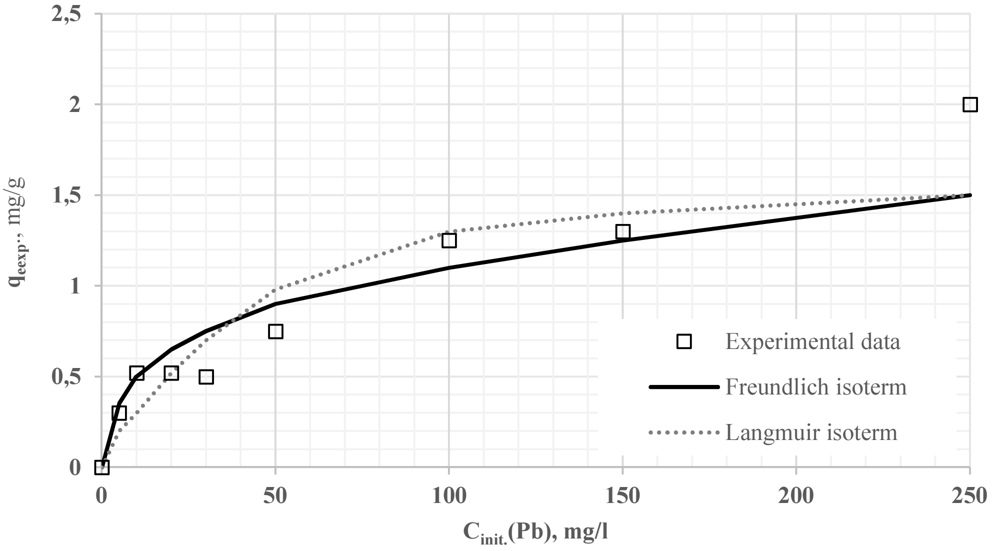

Fig. 4. The comparison between the Langmuir and Freundlich isotherms and the experimental results for lead (Pb)

Table 4. Mathematically modelled and experimental values for sorption capacity and residual concentration

Heavy metals	$C_{init.}$, mg/l	$q_{exp.}$, mg/g	$q_{mod.}$ mg/g	$C_{Lexp.}$, mg/l	$C_{Lmod.}$, mg/l
Langmuir model					
Copper (Cu)	5	0.379	0.245	1.21	2.55
	10	0.473	0.368	5.27	6.32
	15	0.498	0.479	10.02	10.21
	30	0.501	0.549	24.99	24.51
	50	0.525	0.614	44.47	43.86
	100	0.888	0.792	91.13	92.08
	150	0.700	0.812	143.00	141.88
	200	0.917	0.872	190.83	191.28
Freundlich model					
Lead (Pb)	5	0.388	0.359	1.12	1.41
	10	0.543	0.473	4.57	5.27
	15	0.561	0.557	9.39	9.43
	30	0.550	0.734	24.50	22.66
	50	0.773	0.901	42.27	40.99
	100	1.253	1.189	87.47	88.11
	150	1.393	1.398	136.07	136.02
	200	1.853	1.568	181.47	184.32

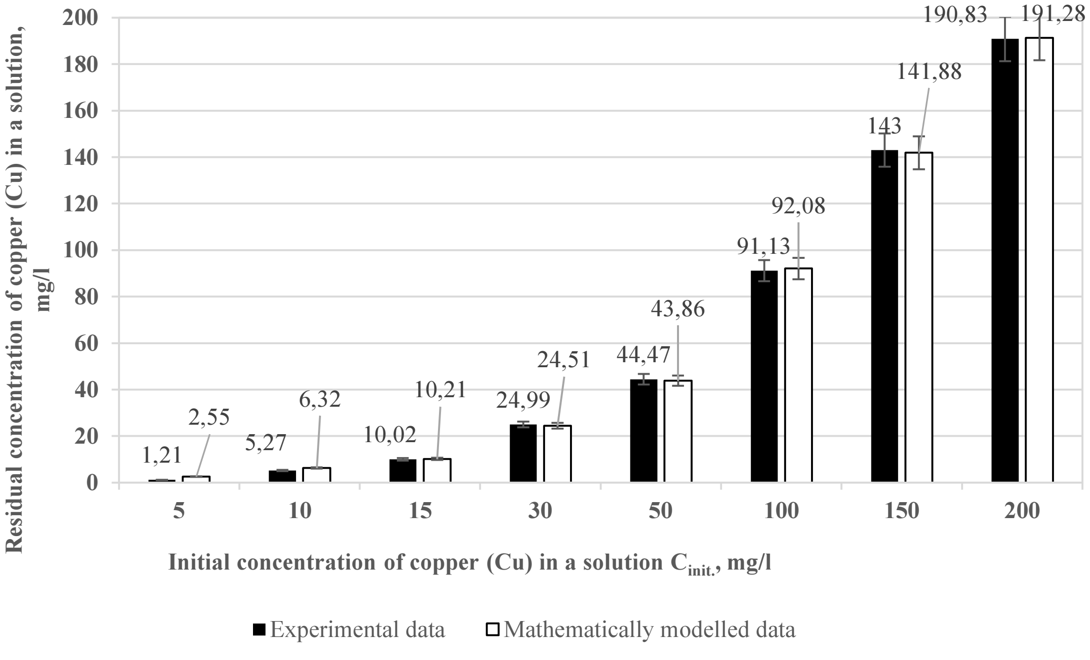

Fig. 5. The comparison between experimental and mathematically modelled residual concentrations of copper (Cu) in a solution

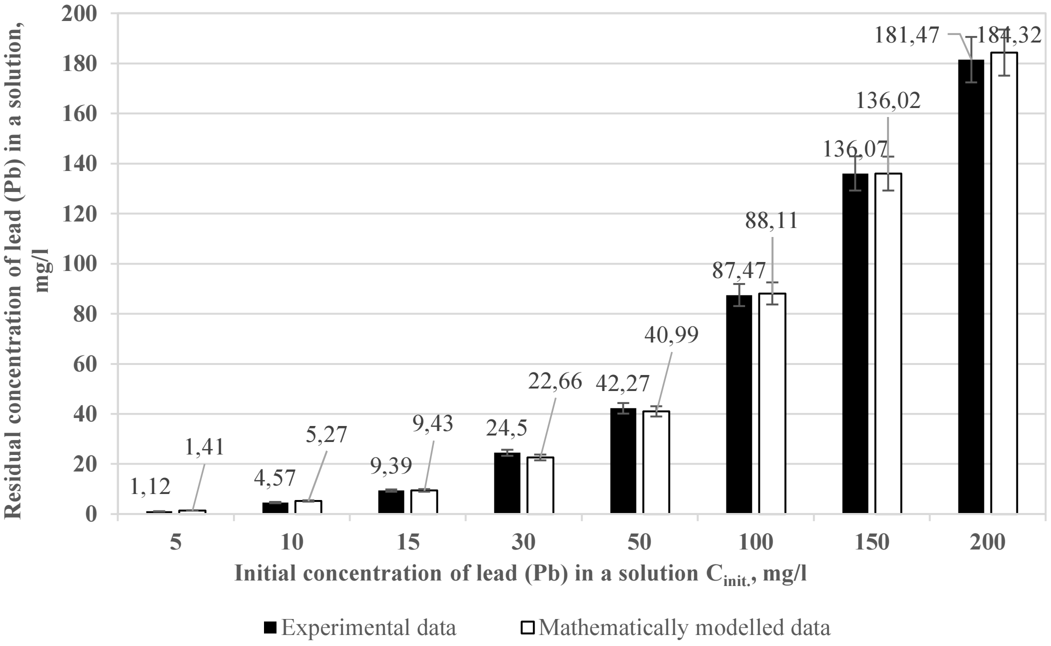

Fig. 6. The comparison between experimental and mathematically modelled residual concentrations of lead (Pb) in a solution

Langmuir isotherm describes the sorption surface as homogeneous whilst the Freundlich isotherm indicates a heterogeneous sorbent surface. It is assumed that different metal ions can be absorbed by different sorbent cell wall groups (Dada *et al.* 2012; Malek, Farooq 1996; Basar 2006; Zheng *et al.* 2009) In the future, a more detailed analysis of biochemical sorbent (coffee grounds) is proposed in order to identify the functional groups for sorption of each metal.

Conclusions

Mathematical modelling has determined that the Lagergren's pseudo-second-order adsorption kinetic model (R^2 = 0.8417–0.9975) better describes the kinetics of the adsorption process of copper (Cu) and lead (Pb) when using coffee grounds as a sorbent than the Lagergren's pseudo-first-order model (R^2 = 0.3665–0.9327) does.

The initial adsorption speed k_2q_e is 1.87–6.17 times higher for removal of Cu and 1.01–4.91 times higher for removal of Pb than when applying the Lagergren's pseudo-first-order model. The adsorption speed is 0.0058–0.4975 and 0.021–0.1661 mg/g per min and the average values of the adsorption rate constants k_2 are 0.117 and 0.037 min^{-1}, respectively.

After conducting the mathematical modelling it was calculated that the Langmuir isotherm better reflects the sorption processes of copper (Cu) (R^2 = 0.950), whilst the Freundlich isotherm – the sorption processes of lead (Pb) (R^2 = 0.925).

The difference between the mathematically modelled and experimentally obtained sorption capacity is 0.059–0.164 mg/l for removal of copper (Cu) and 0.004–0.285 mg/l for lead (Pb). Residual concentrations of metals in a solution showed difference of 1.01 and 0.96 mg/l, respectively. Therefore, it can be said that the chosen models for plotting isotherms represent the adsorption processes of copper and lead very well.

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